

Introduction

Photocatalysis of water splitting has become an active research area and a promising way to capture and store energy from the sun. The main objective is to find materials that can achieve the commercially viable 10% quantum efficiency for hydrogen evolution¹ with solar illumination and no bias voltage. Studies show recent advances in the division of water with visible light in oxynitride photocatalysts, for example, SrTaO₂N semiconductor. In this work we will study the alignment of the valence and conduction bands of the (001) SrTaO₂N / H₂O interface, based on the relaxation of the atomic positions in the interface.

Theoretical Modeling and System

Semiconductor bulk computation (SrTaO₂N): The calculations have been performed using the Wien2k code², which is based on the density functional theory (DFT)³, based and generalized gradient approximation trans-blaha-modified Becke–Johnson (TB-mBJ) exchange-correlation potential was used⁴, to overcome the shortcoming of the underestimation of the energy gaps in both LDA and GGA approximations.

Structure:

Bulk SrTaO₂N (I4mcm): a = 5.65 Å, c = 8.28 Å.

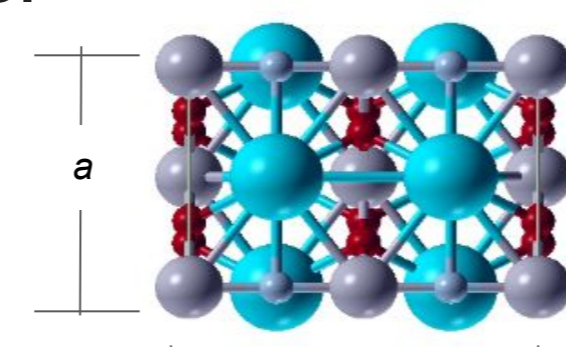


Fig.1. Bulk SrTaO₂N

Liquid water bulk computation (H₂O): The calculations have been performed using the classical Molecular Dynamics computation by DLPOLY⁵ and use the TIP4P⁶ potential to describe the interaction between water molecules using NVT for 100 ps and take snapshots at 300 K.

Structure:

Parallelepiped: 54 H₂O molecules. a = 11.3 Å, c = 13,16 Å

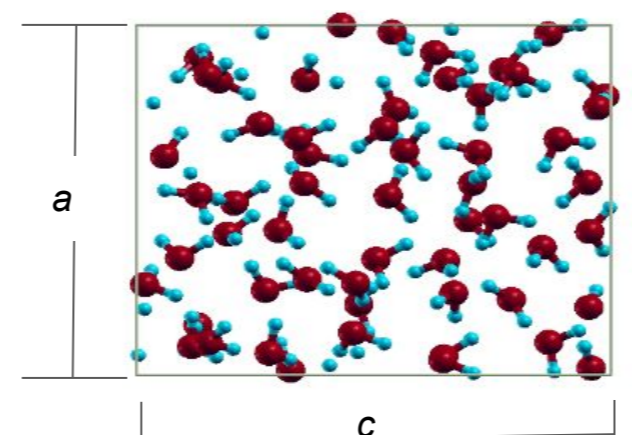


Fig.2. Parallelepiped 54 H₂O

Semiconductor-water interface computation (SrTaO₂N / H₂O): The calculations have been performed using the Quantum Espresso⁷, which is based on the density functional theory (DFT), For the electronic exchange-correlation potential the generalized gradient approximation (GGA), and atomic positions of the unit cell with a Monkhorst-Pack 1 × 1 × 1 k-point grid and plane-wave energy cutoff of 500 eV

Structure:

Interface: Supercell 2x2x3 SrTaO₂N / 54 molecules H₂O (I4mcm): a = 11.3 Å, c = 35.95 Å

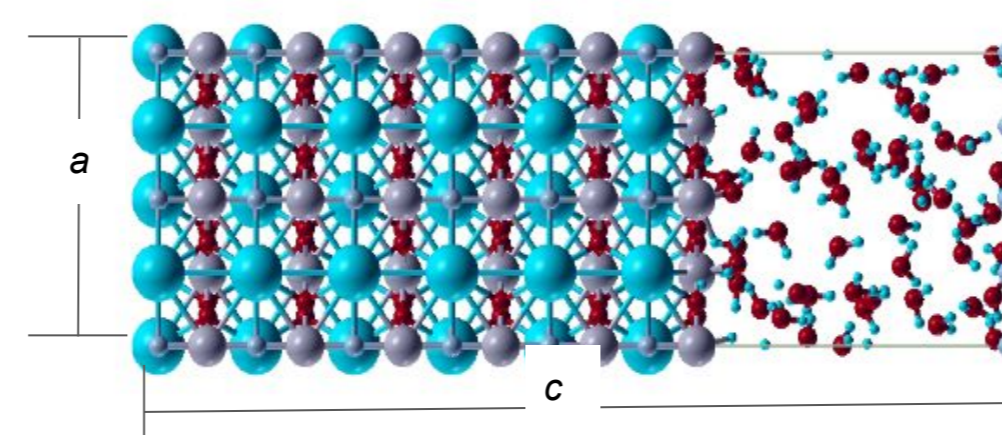


Fig.3. Interface SrTaO₂N / H₂O

Calculation Model

The goal is to compute the CBM band edge position relative to the solution acceptor level (H₂O/H₂ level of liquid water in this work) at the interface, i.e., $E_{c_edge} - A_{edge}$. It was assumed that the band alignment is due to electrostatic effects (electron and ion redistribution near the interface due to Fermi energy realignment). So the energy levels and Hartree potential change by the same amount everywhere in space and their difference remains unchanged⁸. Therefore, the term can be computed by:

$$E_{c_edge} - A_{edge} = (E_{c_bulk} - H_{semi_bulk}) - (A_{bulk} - H_{sol_bulk}) + (H_{semi_edge} - H_{sol_edge}) \quad (1)$$

E_{cbulk} = conduction band minimum (CBM) in the bulk of the semiconductor.

E_{cedge} = CBM at the semiconductor-solution interface.

A_{bulk} = acceptor level (H₂O/H₂ level of liquid water in this work) in the bulk of the solution

A_{edge} = acceptor level at the semiconductor-solution interface.

H_{semi bulk} = Hartree potential in the semiconductor bulk

H_{semi edge} = Hartree potential on the semiconductor side at the semiconductor-solution interface

H_{sol bulk} = Hartree potential in the bulk of the solution.

H_{sol edge} = Hartree potential on the solution side at the semiconductor-solution interface.

References:

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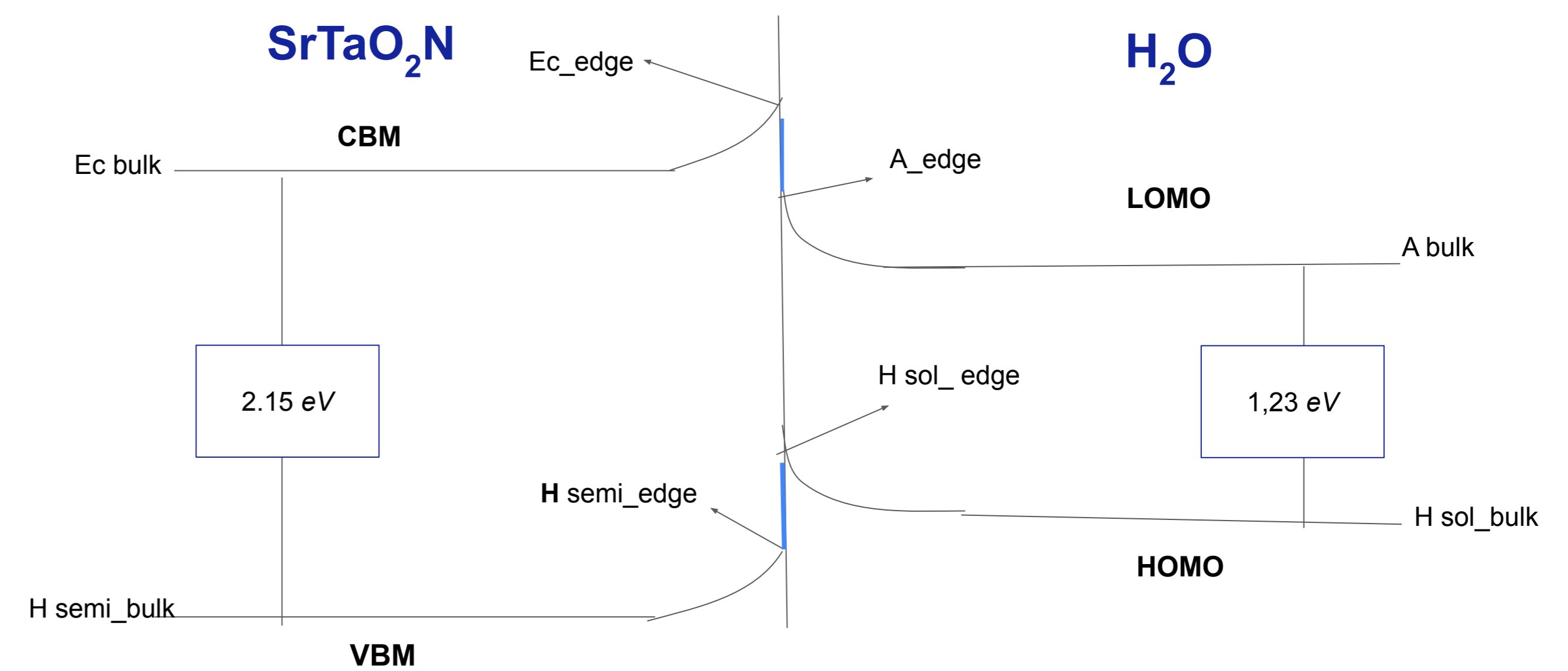


Fig.4 Schematic diagram of the interface band alignment SrTaO₂N / H₂O

Results

The goal is to compute the Hartree potential difference between the semiconductor bulk cell and the liquid water cell in an interfacial slab system. The interfacial cell is constructed by joining several layers of the semiconductor bulk cells in fig. 1 and the liquid water cell in fig. 2 together.⁸

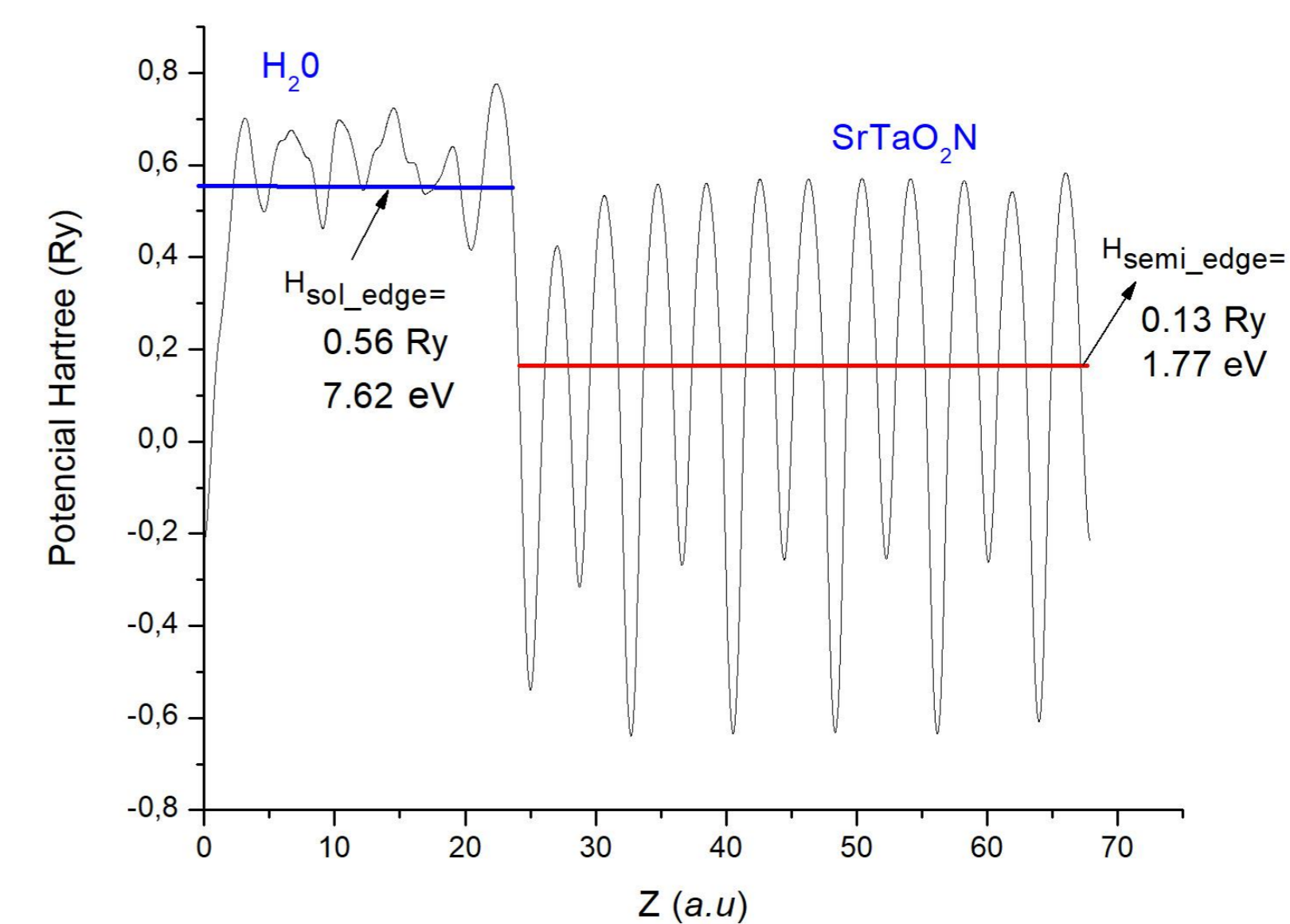


Fig.5. Calculated averaged Hartree potential SrTaO₂N / H₂O Interface. The left side is water and the right side is semiconductor SrTaO₂N. The black solid line is the planar-averaged Hartree potential as a function of cell dimension normal to the interface. The red solid line indicates the planar-averaged Hartree potential of SrTaO₂N, H_{sol}_edge. The blue solid line indicates the planar-averaged Hartree potential of liquid water, H_{sol}_edge.

The photocatalytic water-splitting process is energetically favorable only if the conduction band minimum (CBM) is higher than the H₂/H₂O level and the valence band maximum (VBM) is lower than the O₂/H₂O level. (Here and throughout this paper, “higher” always refers to more negative in the Normal Hydrogen Electrode reference while “lower” always refers to more positive in the NHE reference.) The approach can be generalized to also compute the VBM band edge position relative to the H₂O/O₂ level in water. The VBM can be determined from the position of the edge of the CBM band and the band gap

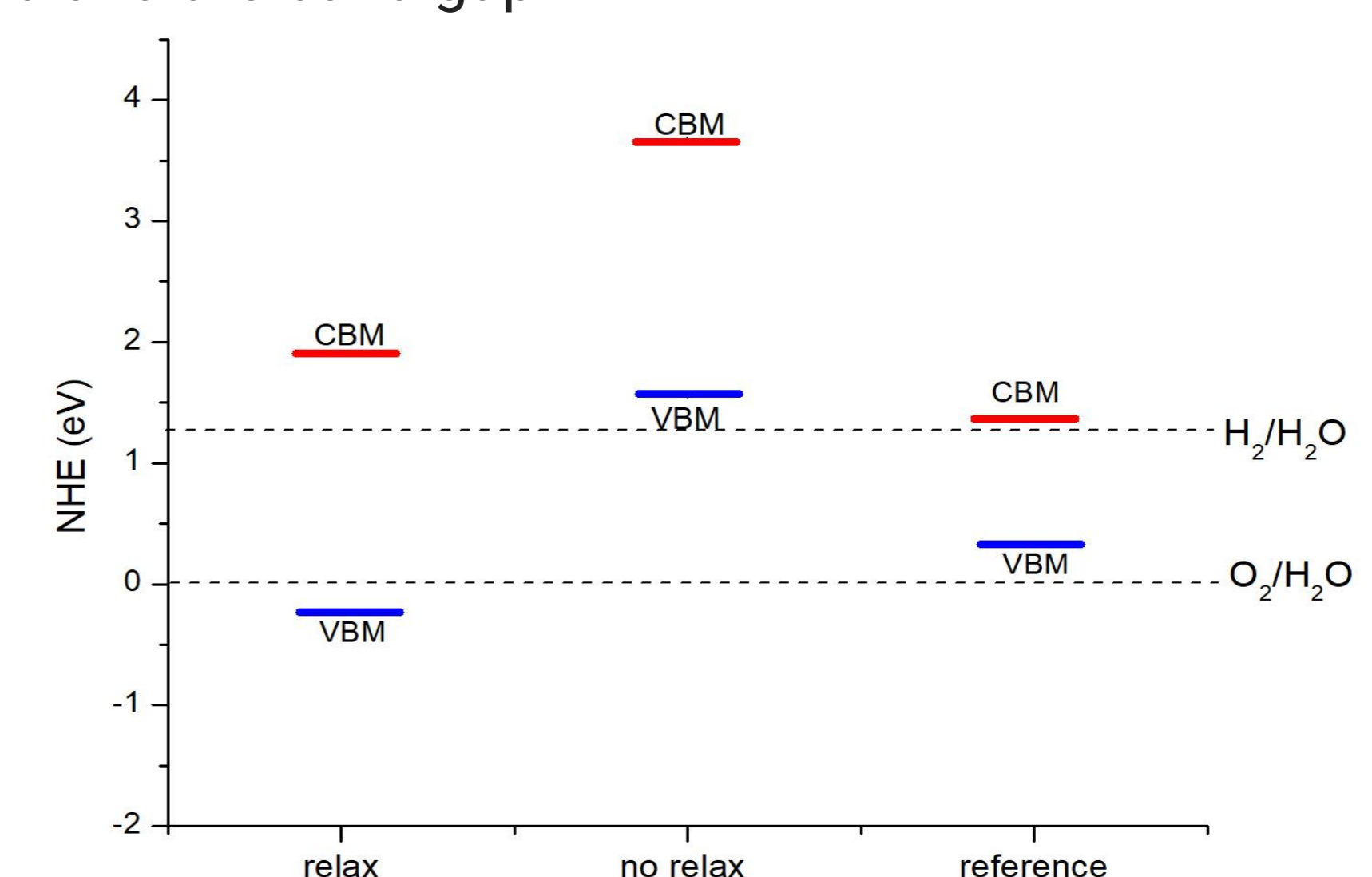


Fig. 6 The position of the edge of the SrTaO₂N band with relaxation, without relaxation of the atomic positions and the reference paper⁸. Solid blue lines indicate VBM levels and solid red lines indicate CMB levels.

With the relaxation of the atomic positions of the atoms of the SrTaO₂N / H₂O interface, it is observed that the semiconductor complies with the GAP and band-edge positions suitable for the photocatalysis of water, compared to the without relaxing interface and the structure of the reference paper⁸.

Conclusions

- In this work, the method was applied to calculate the positions of the border of the CBM band in relation to water, H₂O / H₂ level with relaxation of the atomic positions of the interface atoms.
- The Becke-Johnson (BJ) potential has been used⁴, which made it possible to find a suitable GAP for the band alignment in comparison with the experimental data from the semiconductor side, with a reasonably low calculation cost.
- With the relaxation of the atomic positions of the interface, favorable results are obtained for this compound in the alignment of bands, which places it among the strong candidates to be used in photo-electrochemistry.